



The role of ozone in the plasma-catalytic destruction of environmental pollutants

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ABSTRACT

The destruction of low concentrations of toluene and cyclohexane in air streams using the combination of a novel multistage, non-thermal plasma reactor with either a MnO₂ or a MnO₂-CuO catalyst has been investigated. It is found possible to get complete destruction of the organic pollutant when the plasma and catalyst were combined. The different catalysts produced different outcomes in terms of the residual ozone in the outlet stream and the extent of oxidation to CO₂. Neither of these compounds react to any measurable extent with ozone in the gas-phase nor are they decomposed by the catalyst at the temperature of the experiment. It is deduced that adsorption of ozone onto the catalyst surface and its subsequent dissociation into reactive atomic oxygen species is the key step in the heterogeneous destruction of toluene and cyclohexane.

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1. Introduction

Volatile organic compounds (VOCs) are contaminants that are emitted from a wide range of sources including semiconductor manufacturing plants and chemical processing plants. Their presence in air contributes significantly to photochemical smog production; VOCs also pollute soil, surface water and groundwater. Emission of VOCs into the atmosphere is detrimental to both human beings and the environment. The remediation of dilute VOCs from waste gas streams is both a health and environmental concern. It is necessary to remove VOCs from waste gas streams due to increasing emission control legislation. Toluene is widely used in many applications, such as in the pharmaceutical industry and it is an important feedstock in chemical processes. It is often used as a solvent because of its excellent ability to dissolve substances. Toluene is also used to make spray and wall paints, medicine, dyes, explosives, detergents, spot removers, lacquers, adhesives, rubber, and antifreeze. Cyclohexane is a widely used non-polar solvent and is also a raw material for intermediates used in the production of nylon.

Non-thermal plasma processing can be more efficient in decomposing VOCs than conventional technologies, such as catalytic combustion or thermal incineration, as no energy is wasted in heating the gas molecules [1]. A disadvantage, however,

of plasma technology is often incomplete oxidation, leading to potentially toxic by-products [2]. This problem can be solved by combining a non-thermal plasma system with a catalyst [2,3]. This is because there is an increase in reaction time due to adsorption of intermediates and contaminants on the catalyst surface, resulting in a shift towards total oxidation [2]. There is also preferential consumption of active species by surface reactions on the catalyst instead of undesired gas-phase reactions [2].

In recent years, this hybrid plasma-catalysis process, combining the use of plasma and catalysis methods has been extensively investigated and developed [2,4–8]. It is now well established that the performance of non-thermal plasma systems for the removal of low concentrations of pollutants can be improved particularly by the addition of catalyst material into the discharge region of the reactor [9]. The performance of a plasma-catalytic reactor has been found to be superior to a plasma reactor for a range of VOCs [3]. Advantages of using plasma-catalysis systems over plasma alone include enhanced conversion of pollutants, lower energy input giving improved energy efficiency for the plasma process, higher CO₂ selectivity and extended catalyst lifetime [9,10]. A synergistic effect has been reported in some cases for the plasma-catalytic decomposition of VOCs, where the effect of the combined treatment is found to be higher than the sum of the individual steps [11–13]. The excited species produced by the non-thermal plasma have a high catalytic ability; their concentration increases with increasing plasma energy which means that the synergic effect also increases with energy [12]. Another advantage is that the VOCs can be decomposed at ambient temperatures so there is

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no need to heat the catalysts [12]. In addition, the catalyst reduces the formation of by-products as well as increasing the removal efficiency [12]. The main oxidising species formed by non-thermal plasma in oxygen-containing gas streams is ozone due to the dissociation of oxygen molecules [14]; it can either react directly with the VOCs or decompose on the catalyst to give reactive atomic oxygen in surface sites [15].

There are two types of arrangements for these hybrid plasma-catalysis systems, sometimes known as one- and two-stage configurations. The role of the non-thermal plasma is highly dependant on the configuration used [16,17]. In the one-stage configuration, the catalyst is placed directly in the discharge region allowing the plasma to directly activate the catalyst. In the two-stage configuration, the catalyst is placed downstream from the plasma reactor. This means that only long-lived species such as ozone and some stable organic intermediates produced by the plasma will be involved in reactions with the catalyst. Synergistic effects are thought to be limited to when the catalyst is placed inside the discharge region (one-stage system) [9]. In a one-stage configuration, the synergistic effect will be greater due to the increase in concentration of short-lived excited species on the surface of the catalyst and the effect of photons and electrons generated in the plasma.

The presence of highly reactive species and electrons in the plasma trigger physical changes in the catalyst material, consequently affecting the VOC surface adsorption. Plasma-catalytic systems have been shown to exhibit zero-order kinetics during VOC decomposition, indicating the importance of surface reactions [18]. The addition of a catalyst in the one-stage configuration may change the discharge characteristics and in both configurations it can change the chemical reactions involved in the processing [10]. In a one-stage configuration, electron-induced processes, surface discharges and short-lived radicals are potential active species as opposed to long-lived species in a two-stage configuration. In a two-stage configuration, by moving the catalyst away from the plasma where the excited species are created, it is possible to look at the effect of the lifetimes of various radicals and excited species on the destruction of pollutants [12]. In the one-stage configuration, the catalysts are directly activated by the non-thermal plasma at lower temperatures than applies in conventional thermal catalysis [17], even at temperatures as low as room temperature where normally thermal catalysis does not occur [16]. Additional advantages of the combined plasma-catalysis over conventional thermal catalysis include rapid start-up and shutdown and simple construction requiring no heat insulation [17].

It is well known that non-thermal plasma in air can produce high levels of ozone [13]. Although decomposition of ozone to oxygen is a thermodynamically favoured process, ozone is stable up to 100–250 °C. At lower temperatures, a catalyst is necessary for ozone decomposition, producing active species on the catalyst surface, which may induce secondary oxidation reactions. Due to its long lifetime, ozone is of importance in both one- and two-stage plasma systems [15]. In the two-stage configuration, ozone may still be present in significant concentrations and partial oxidation of the VOCs may take place with ozone in the gas-phase [17] and also over a downstream catalyst bed [2,19–22]. Holzer et al. [2] have suggested that in a two-stage configuration hydrocarbon species may be adsorbed on the catalyst deactivating its effectiveness for ozone decomposition. It is believed that the conversion of VOCs is mainly due to ozone acting either directly or indirectly via adsorption or decomposition on catalyst surfaces, leading to the formation of strongly oxidizing species, such as atomic oxygen [9,14].

This work tries to identify the mechanism of VOC destruction using plasma-catalysis by looking at the action of plasma and ozone separately on the decomposition of toluene and cyclohexane

including the addition of a catalyst using a novel, energy-efficient, multistage plasma reactor [13,23]. Ozone has a longer lifetime than other plasma-generated species, so it is thought that only ozone will be present in this system when the VOC is injected into the system downstream of the plasma cells. This work shows that ozone on its own is incapable of destroying pollutants in the gas-phase but when combined with a catalyst, successful destruction is seen.

2. Experimental

This work is carried out in a similar manner to that described previously [13]. A schematic of the system is shown in Fig. 1. The apparatus consists of three plasma reactors in series contained in a gas-tight box with external power supplies. Each plasma cell contains two copper mesh electrodes spaced by a distance of 1.65 cm, the copper mesh area of each electrode being 63 cm². Between the electrodes is an air-permeable fixed bed of glass beads (6 mm in diameter). The spacing between the cells is 3.7 cm and each cell is mounted in such a way as ensures that the gas passes through the cell and does not by-pass it. Each plasma cell is individually powered by a high voltage, high frequency, neon sign transformer power supply. The output from the neon sign transformer is 10 kV, 30 mA at full supply voltage with a frequency of 21 kHz. The input voltage of these power sources is controlled by a variac (Zenith Electric Company Ltd.). The input or wall-plug energy consumption is measured by a plug-in power and energy monitor (Prodigit Electronics, 2000MU). Separate experiments with high voltage and current probes indicate that the plasma power is ~20% of the input electrical power for this system. We choose to reference our cell performance to the input power as this is a true measure of the “real” performance of the system in terms of energy consumption.

Two different catalysts are used in this work. The first catalyst is Honeycyle ZA (Nichias Corporation) (catalyst A) which is an ozone destruction catalyst. It is a MnO₂ catalyst supported on an aluminium honeycomb monolith of thickness 2 cm. The second catalyst tested (catalyst B) is Moleculte (Molecular Products Limited). This is a MnO₂-CuO catalyst capable of decomposing ozone and oxidising carbon monoxide. The catalyst has a surface area of 20–30 m² g⁻¹, size 4–6 mesh and a total volume of 154 cm³ is loaded into a polycarbonate filter box. Either or both catalysts may be placed downstream after the plasma cells as required, as shown in Fig. 1, and are unheated.

In the experiments, a mixture of air and the vapour of the VOC pass through the reactor controlled by mass flow controllers

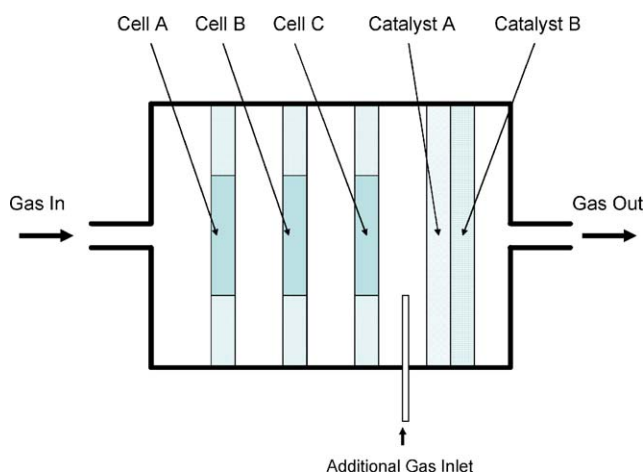


Fig. 1. Schematic diagram of the reactor.

(MFC), maintained at a pressure of 1 bar, to give a total flow rate of 1–10 L min⁻¹. Toluene or cyclohexane is introduced into the gas flow by passing a certain amount of nitrogen (controlled by an MFC) through a bubbler containing the appropriate liquid. The toluene and cyclohexane concentrations are determined by FTIR spectroscopy, as previously [13].

3. Results

3.1. Toluene

These experiments were carried out for an initial toluene concentration 70 ppm in air at a total flow rate of 10 L min⁻¹. The input voltage to the reactor is 45 V, and the input power is 57 W. Toluene is passed through the three plasma cells and the effect of using the two different catalysts, placed downstream of the cells, is investigated. Four different configurations are investigated with the (1) catalyst alone, (2) plasma alone, (3) plasma with Honeycyle ZA (catalyst A), (4) plasma with Moleculte (catalyst B) and (5) plasma with both catalysts together. The final concentrations of toluene, CO, CO₂, O₃ and N₂O are measured and are given in Table 1. It has previously been shown [13,23] that a unique property of this multistage plasma reactor is that it achieves high destructions without any detectable production of NO_x (NO + NO₂ + HNO₃) (<0.01 ppm) over the range of energies used in these experiments.

Using either of the catalysts alone, without plasma, gives no destruction of toluene. Modest destruction of 36% is seen when the plasma is used on its own, with high levels of ozone and a small amount of N₂O. CO and CO₂ also being formed, showing that toluene is being oxidised. Complete removal of toluene is seen when the catalysts are used, either separately or together but the distribution of the products varies depending on which catalyst is used. When the plasma is used in conjunction with catalyst A (Honeycyle ZA) high levels of CO and CO₂ are seen but no ozone is detected in the output stream showing that this catalyst is an efficient catalyst for both ozone and toluene removal. When catalyst B (Moleculte) is used with the plasma, higher levels of CO₂ and reduced CO are seen and also higher levels of ozone than with catalyst A. This means that catalyst B is an effective catalyst at converting toluene into CO₂ but is less efficient than catalyst A at removing ozone. When both catalysts are used together with the plasma cells activated, total removal of both toluene and ozone is seen and good conversion to CO₂. It is worth noting that in experiments (1) and (2), higher destruction of toluene could have been achieved if the input energy had been increased, however for the purpose of this work, we needed to work at reduced destructions to determine the effect of different catalysts from the observed changes in the destruction of toluene and distribution of by-products. We have shown [23] that 100% destruction of toluene can be achieved using three plasma cells without a catalyst at higher electrical energies.

This next series of experiments investigates the separate role of ozone in the destruction of toluene with and without a catalyst. In experiment (6), ozone is created by discharging air alone in the

Table 2

Concentration of end-products using ozone to destroy toluene.

	Concentration (ppm)				
	Toluene	CO	CO ₂	O ₃	N ₂ O
(6) Ozone + toluene	70	0	0	766	12
(7) Ozone + toluene + catalyst A	0	16	25	0	13

three plasma cells, and then 70 ppm of toluene is injected into the system after the 3rd plasma cell (C) using the additional inlet shown in Fig. 1 to determine whether any destruction of toluene by ozone is seen. The total flow rate was kept at 10 L min⁻¹. No catalyst is present. In the final set of experiments (7), the same methodology for (6) is followed but the Honeycyle catalyst, catalyst A, is placed into the system and the interaction of ozone, toluene on the catalyst is investigated. The results are given in Table 2.

When toluene is injected into the system downstream of the plasma cells, with no catalyst present (6), no destruction of toluene is seen. High levels of ozone are detected but no CO or CO₂ is formed indicating that there is no oxidation of toluene. This indicates that ozone cannot destroy toluene in the gas-phase. When catalyst A (Honeycyle) is used in this system (7), total destruction of both toluene and ozone is seen with results similar to (3) where the toluene was also passed through the plasma discharge. It should be remembered that the earlier experiment (1) showed that the catalyst on its own had no effect on the destruction of toluene at the ambient temperature of the experiment. This demonstrates that it is the combined effect of ozone and the catalyst that is destroying toluene. The increased yield of CO and CO₂ in experiment (3) compared to (7) may indicate that toluene is being decomposed both in the plasma cells and on the surface of the catalyst. Similar results were obtained when this experiment (7) was repeated using Moleculte, catalyst B.

The carbon balances (ratio of carbon atom concentration in gaseous end-products to that in the starting material) obtained from this work are very low; plasma alone (2) yields 20%; plasma with catalyst A (3) 26%; plasma with catalyst B (4) 16%; plasma with both catalysts (5) 25% and ozone with catalyst A (7) 8%.

3.2. Cyclohexane

An additional set of experiment were performed in which cyclohexane was used instead of toluene to investigate any effects that might be specific to the VOC. The experiments were carried out with an initial cyclohexane concentration of 88 ppm and a total flow rate of 1 L min⁻¹. The input voltage to the reactor is 30 V, and the input power is ~10 W. The same total flow rate was used in all experiments. The results are given in Table 3.

It should be noted that these conditions are not identical to those used for the destruction of toluene. The reduced flow rate will increase the residence time and decrease the loading on the catalyst surface but the reduced input power (10 W versus 57 W) will decrease the conversion of cyclohexane in the plasma (24%

Table 1

Concentration of the end-products in the plasma destruction of toluene with catalysts A (Honeycyle ZA) and B (Moleculte).

	Concentration (ppm)				
	Toluene	CO	CO ₂	O ₃	N ₂ O
(1) Catalyst alone	70	0	0	0	0
(2) Plasma alone	45	16	19	1327	23
(3) Plasma + catalyst A	0	48	80	0	18
(4) Plasma + catalyst B	0	8	72	117	21
(5) Plasma + catalyst A + catalyst B	0	10	110	0	18

Table 3

Concentration of the end-products in the plasma destruction of cyclohexane with catalysts A (Honeycyle ZA) and B (Moleculte).

	Concentration (ppm)				
	Cyclohexane	CO	CO ₂	O ₃	N ₂ O
(1) Plasma alone	67	11	16	1143	18
(2) Plasma + catalyst A	0	37	102	0	20
(3) Ozone + cyclohexane	88	0	2	985	6
(4) Ozone + cyclohexane + catalyst A	0	22	68	0	24

compared with 36% for toluene) and reduce the yield of the ozone. However, the addition of catalyst A achieves complete destruction and high selectivity for CO₂ production (experiment (2)). In the absence of a catalyst (experiment (3)), ozone alone cannot destroy cyclohexane as was found for toluene. The addition of the catalyst (experiment (4)) promotes complete destruction of cyclohexane.

4. Discussion

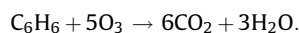
Van Durme et al. [24] have reported similar observations in a two-stage plasma-catalyst configuration using a CuO/MnO₂/TiO₂ catalyst with a corona discharge. They studied the destruction of 0.5 ppm of toluene in air at an energy density of 20 J L⁻¹ and a gas flow of 10 L min⁻¹ and found that only 2% of the toluene was removed with no catalyst compared to 78% with the catalyst. In pure air (i.e. no toluene present), 92 ppm of ozone was seen when the plasma is activated, which reduced to 5 ppm when the catalyst system was applied. They also observed that increased humidity levels reduced the toluene destruction attributed to blocking of active sites on the catalyst surface by water molecules.

Reaction of ozone with toluene in the gas-phase is very slow ($1.2 \times 10^{-20} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [25]) particularly compared to the reaction of toluene with atomic oxygen ($5.7 \times 10^{-12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ [25]) explaining the observation that no destruction of the VOC is seen with ozone in the absence of the catalyst (experiments (6) for toluene and (3) for cyclohexane). So we can deduce that the mechanism of the process that we are observing is heterogeneous and is related to the adsorption and dissociation of ozone on the catalyst surface. This gives rise to atomic oxygen on the surface and the subsequent conversion of the VOCs by surface reactions as discussed by Roland et al. [9]. It is well known that the surface of a catalyst can be activated by high energy particles, such as electrons, excited molecules or radicals [26]. Roland et al. [9] also speculate that oxidation improvements are related to the porosity of the catalyst structure. If a porous material is introduced into the discharge, part of the reactivity is transferred into the absorbed phase, corresponding to the presence of organic intermediates on the surface [27]. Roland et al. [15] study the role of ozone in both a one- and two-stage plasma-catalysis system for the destruction of toluene. They tested the inherent potential for ozone decomposition by various catalysts. γ -Alumina was found to catalyse this reaction where the oxidation of organic compounds absorbed on γ -alumina in a two-stage system can be explained by the formation of active oxygen due to the catalysed ozone decomposition [15].

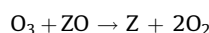
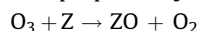
Einaga and Futamura [28] studied the catalytic oxidation of benzene with ozone over various catalysts. They used a MnO₂/Al₂O₃ catalyst and found that Mn is crucial for obtaining catalytic activity but that the rate of benzene oxidation is not sensitive to the amount of loaded Mn. They also found that the surface area of the support is an important factor for catalytic activity. They suggest that it is the active oxygen species, formed from ozone, that are responsible for benzene oxidation on manganese oxide catalysts [28]. Kim et al. [16] also believe that the main oxidising species for benzene decomposition in a plasma-catalysis reactor are probably oxygen atoms and ozone (rather than OH radicals). In a separate study, Einaga et al. [29] looked at the decomposition of benzene in air using a silent discharge reactor combined with a MnO₂ catalyst. They found that benzene conversion is greatly enhanced when the MnO₂ catalyst is combined with the plasma and attribute this enhanced decomposition of benzene to the role of ozone interactions with the catalyst [29]. They state that solid manganese oxides accelerate the decomposition of ozone to oxygen in the gas-phase. During ozone decomposition, active oxygen species (such as O(³P), O(¹D), O⁻, O₃ and possibly O₃⁻) may be formed and show higher reactivity towards hydrocarbon than ozone itself. It is these oxygen species formed during ozone decomposition that may be

responsible for benzene decomposition on MnO₂ [29]. They also find that the oxidation state of manganese has a strong effect on the oxidation of benzene to CO₂. The use of a CuO–MnO₂ catalyst (experiment (4)) is well known to assist the oxidation of CO into CO₂ at ambient temperatures as we observe here [30]. Similar conclusions about the role of ozone decomposition on a manganese catalyst have been drawn by Einaga and Futamura [31] for the decomposition of cyclohexane by ozone.

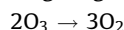
Naydenov and Mehandjiev [32] also studied the complete oxidation of benzene on MnO₂ by ozone. They propose the following stoichiometric equation for the complete catalytic oxidation of benzene on oxide catalysts in the presence of ozone as:



The suggest that the heterogeneous catalytic decomposition of ozone takes place according to the following mechanism, similar to that proposed by Li et al. [33,34],



giving an overall decomposition of ozone:



where Z is an active site on a catalytic surface. They find that the use of ozone lowers the reaction temperature for benzene oxidation over a MnO₂ catalyst. It is thought that the apparent activation energy is three times lower in the presence of ozone, suggesting that the rate determining state is the catalytic ozone decomposition [32]. Demidyuk and Whitehead [35] have studied temperature of the plasma destruction of toluene in conjunction with a catalyst of MnO₂ supported on γ -alumina and deduce that the enhancement in destruction obtained using the catalyst is due to the formation of additional active centres on the catalyst surface rather than the reduction of the activation energy. They suggest that in this case the mechanism of the plasma activation of the catalyst involves changes in the oxidation states of the manganese ions. Radhakrishnan et al. [36] state that ozone decomposition on a MnO_x/Al₂O₃ catalyst proceeds by electron transfer from the Mn site to adsorbed ozone, which produces reactive atomic oxygen on the surface. During desorption of the oxygen species Mn is reduced back to its Mn²⁺ state.

Kim et al. [37] propose a more general mechanism for the plasma-catalyst decomposition of VOCs, stating that although the detailed mechanism is still unclear at this stage, the synergistic effect can be explained by the involvement of the catalyst surface activated by plasma. They note that many possible mechanisms, such as ozone, UV, local heating, changes in work function, activation of lattice oxygen, plasma-induced adsorption/desorption, direct interaction of gas-phase radicals with the catalyst surface and the adsorbed molecules, have been proposed [37]. The main models for the heterogeneous chemistry that they believe to contribute to plasma-catalysis of VOCs are the Langmuir–Hinshelwood model, in which both reactants are absorbed on the surface and then migration to the active site occurs, and the Eley–Rideal model, in which one reactant is adsorbed on the surface and the other exists in the gas-phase [37]. The similarity that we observe in the decomposition efficiencies of cyclohexane and toluene suggests that either a Langmuir–Hinshelwood type of mechanism involving surface-adsorbed oxygen atoms and the hydrocarbon or an Eley–Rideal mechanism in which the surface-adsorbed species is atomic oxygen is involved. The reaction of ozone with toluene whilst slow in the gas-phase is facilitated by the addition of ozone to the aromatic π -bonds whereas there is no such possibility for the reaction of the unsaturated cyclohexane with ozone which can only be oxidised by atomic oxygen. Thus the reactive species in this processing is atomic

oxygen produced on the surface of the catalyst by decomposition of ozone. It is not possible from the present results to deduce whether the hydrocarbon reacts in the gas-phase or on the surface (i.e. Eley–Rideal or Langmuir–Hinshelwood). It is clear that there is an excess of ozone in the plasma–catalysis experiments and that 100% destruction is easily achieved for both toluene and cyclohexane indicating that lower ozone levels (and hence lower input energies) could have achieved a similar outcome.

Low carbon balances similar to the present studies are also seen in other work. Einaga et al. [29] see a low carbon balance when they study the decomposition of benzene; they state that the carbon balance is imperfect due to adsorption and desorption of gaseous intermediates on MnO₂, which is likely to be what is happening in this work, especially as we are using a similar catalyst although the production of solid carbon-containing products cannot be discounted. They also detect similar carbon-containing, gaseous end-products to this work.

5. Conclusions

There is still much speculation over the specific mechanism for plasma-catalysis destruction of VOCs. However, this work shows that plasma-generated ozone alone cannot destroy pollutants, instead it is the combination of ozone with a catalyst that gives high decomposition of pollutants via the adsorption of ozone onto the catalyst surface and its subsequent dissociation into atomic oxygen species which participate in heterogeneous reactions giving efficient destruction of the toluene and cyclohexane.

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